SUPPLEMENTARY MATERIAL

Hypervalency Avoided: Simple Substituted BrF_3 and BrF_5 Molecules.

Structures, Thermochemistry, and Electron Affinities
of the Bromine Hydrogen Fluorides HBrF_2 and HBrF_4

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Table S1. Harmonic vibrational frequencies (cm^{-1}) and their infrared intensities (km/mol, in parentheses) for structure **2na**, the lowest energy structure of HBrF_2 .

Symmetry	BHLYP	B3P86	B3LYP	BP86	BLYP
a'	83(7)	88(8)	81(7)	89(8)	82(7)
a''	97(33)	105(38)	96(36)	108(40)	99(40)
a'	116(1)	123(1)	112(1)	129(3)	115(2)
a'	282(199)	325(182)	302(180)	347(164)	323(162)
a'	697(57)	661(55)	643(52)	613(58)	594(54)
a'	4239(225)	4093(199)	4049(189)	3921(174)	3884(167)

Table S2. Harmonic vibrational frequencies (cm^{-1}) and their infrared intensities (km/mol, in parentheses) for structure **2aa**, the lowest energy structure of HBrF_2^- .

Symmetry	BHLYP	B3P86	B3LYP	BP86	BLYP
a'	51(3)	55(2)	54(2)	55(2)	54(2)
a'	260(29)	252(15)	240(14)	225(10)	210(10)
a'	408(211)	421(141)	404(142)	409(101)	393(104)
a''	1137(150)	1097(128)	1080(129)	1050(111)	1036(112)
a'	1156(78)	1128(72)	1108(72)	1088(69)	1072(70)
a'	2722(4441)	2592(3855)	2590(3848)	2443(3353)	2437(3356)

Table S3. Harmonic vibrational frequencies (cm^{-1}) and their infrared intensities (km/mol, in parentheses) for structure **4na**, the lowest energy structure of HBrF_4 .

Symmetry	BHLYP	B3P86	B3LYP	BP86	BLYP
a''	61(2)	73(20)	68(2)	87(1)	79(1)
a'	67(20)	82(19)	73(17)	93(6)	84(8)
a'	155(12)	152(9)	143(12)	154(6)	141(7)
a'	267(105)	244(94)	232(92)	223(78)	205(79)
a''	256(5)	242(6)	237(6)	227(6)	222(6)
a'	369(3)	332(4)	322(4)	281(8)	270(6)
a'	493(547)	506(176)	489(225)	471(39)	455(40)
a'	562(36)	565(387)	538(337)	556(300)	534(325)
a''	486(183)	536(159)	506(162)	603(136)	557(141)
a'	647(169)	655(178)	626(155)	603(98)	580(95)
a'	732(32)	682(1)	659(8)	759(246)	690(205)
a'	4095(224)	3832(240)	3837(212)	3458(245)	3526(204)

Table S4. Harmonic vibrational frequencies (cm^{-1}) and their infrared intensities (km/mol, in parentheses) for structure **4aa**, the lowest energy structure of HBrF_4 .

Symmetry	BHLYP	B3P86	B3LYP	BP86	BLYP
a''	22(0)	24(0)	23(0)	23(0)	22(0)
a'	50(1)	51(2)	50(1)	50(2)	49(2)
a''	106(0)	96(0)	95(0)	83(0)	82(0)
a'	189(7)	166(3)	161(3)	148(1)	143(1)
a'	259(17)	247(14)	240(14)	228(14)	219(15)
a'	282(12)	270(13)	259(11)	232(19)	223(16)
a'	372(128)	372(126)	356(122)	366(98)	351(96)
a''	506(457)	510(368)	471(5)	452(4)	469(276)
a'	509(7)	488(4)	493(364)	486(284)	435(5)
a''	956(155)	988(128)	963(129)	979(107)	958(108)
a'	996(76)	1034(74)	1008(74)	1027(69)	1005(70)
a'	3307(3436)	2964(3237)	2985(3181)	2685(2966)	2707(2936)